ATTACHMENT A TO APPENDIX C. BENZYL ALCOHOL SUPPLEMENTAL INFORMATION

Introduction

To support an approach to biological testing for benzyl alcohol during remedial design, this attachment summarizes information about benzyl alcohol and changes to analytical methods that may affect the link between concentrations and potential toxicity. The Pre-Design Investigation Quality Assurance Project Plan (PDI QAPP) will include a proposed approach to biological testing.

Benzyl alcohol is an aromatic organic alcohol that is present in a wide variety of plants, including edible fruits, teas, and flowering plants. It is also produced industrially for use as a solvent, a preservative, and feedstock for the manufacture of other chemicals and is a transient intermediate by-product of toluene oxidation. Benzyl alcohol is readily biodegradable, with 94% degradation measured in a standard 28-day test conducted under aerobic conditions (NIH 2019), and thus is not persistent in sediment. It is not hydrophobic, with an octanol-water partition coefficient range of 1.00 to 1.16 (EPA 1989; Montgomery 2000). Therefore, benzyl alcohol is of low concern for bioaccumulation (EPA 1989).

Washington State's benzyl alcohol sediment cleanup objective (SCO) (57 µg/kg) was established in 1986 based on the apparent effects threshold for the Microtox® bioassay. Benzyl alcohol was rarely detected in sediment collected in Washington State, including in the Lower Duwamish Waterway (LDW), prior to 2010 (Fourie and Fox 2016). LDW locations with benzyl alcohol data are shown on Map A-1. In the remedial investigation/feasibility study (RI/FS) dataset for the LDW (Windward 2010; AECOM 2012), benzyl alcohol was rarely detected in surface and subsurface sediment samples with reporting limits (RLs) that ranged from 0.9 to 4,200 µg/kg, with a median of 33 µg/kg,¹ and there were very few detected results that exceeded the benzyl alcohol SCO (Table A-1, Figure A-1). However, investigations conducted since 2010 have reported greater detection frequencies and exceedances of the SCO in sediment collected throughout Washington State, including in the LDW (Fourie and Fox 2016). Benzyl alcohol concentrations, total organic carbon (TOC), and percent fines are provided in Table A-2 for the upper reach locations that only have exceedances of the benzyl alcohol remedial action level (RAL).

¹ RLs are sample specific and are affected by sample dilution. The highest RL values reflect samples that were diluted in order to get target semi-volatile organic compound concentrations within calibration ranges.



Table A-1
Summary of LDW-wide Surface and Subsurface Sediment Benzyl Alcohol Data

Date Range	No. of Sediment Samples	Benzyl Alcohol Detection Frequency	Number of Non-Detect Locations with Reporting Limits greater than SCO	Number Locations with Detected SCO Exceedances	Detected SCO Exceedance Frequency
RI/FS Dataset					
1990–1994	99	0%	5	0	0%
1995–1999	649	1.5%	102	0	0%
2000–2004	125	8%	9	1	0.8%
2005–2009	572	4%	46	24	4.2%
Post-FS Datase	et				
2010–2014	865	64%	21	332	38.4%
2015–2018	155	44%	4	24	15.4%

Notes:

FS: feasibility study

LDW: Lower Duwamish Waterway

RI: remedial investigation

SCO: sediment cleanup objective

Table A-2
Surface sediment Samples in the Upper Reach that Exceed the RAL for Only Benzyl Alcohol

Sample Name	Benzyl Alcohol Conc. (µg/kg)	Benzyl Alcohol RAL (µg/kg)	TOC (% dw)	Fines (% dw)
LDW18-SSOT-DeltaMarine	600	114	2.40	78.6
LDW-SS2085-A	360	114	2.35	77.7
LDW-SS2089-A	360	114	3.53	89.3
LDW-SS2089-D	300	114	3.31	88.8
LDW-SS2083-A	290	57	2.66	92.0
LDW-SS2082-U	280	57	4.00	94.2
LDW-SS2214-A	280 J	114	2.70	94.5
LDW-SS2092-A	250	114	1.99	71.7
LDW-SSBDC2-U	230	114	2.35	57.4
LDW-SS2094-D	220	114	2.46	60.2

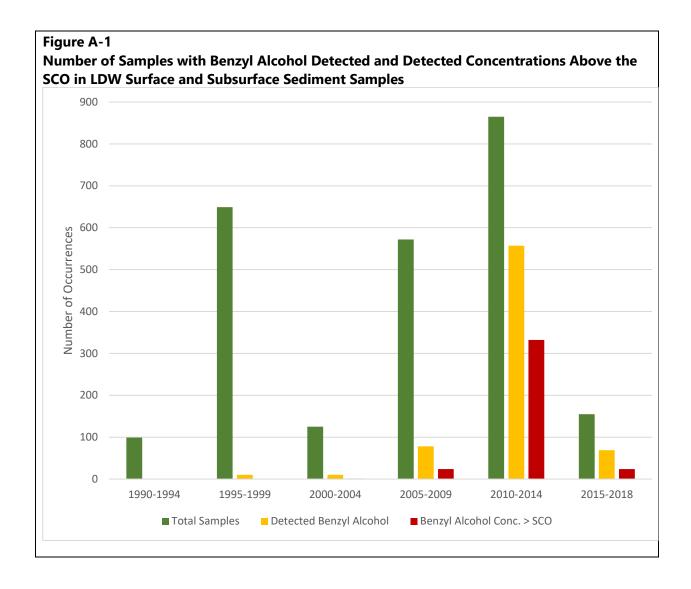
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Sample Name	Benzyl Alcohol Conc. (µg/kg)	Benzyl Alcohol RAL (µg/kg)	TOC (% dw)	Fines (% dw)
LDW-SS2097-D	220	114	2.17	73.6
LDW-SSBDC2-D	200	57	2.23	60.8
RP-24	200 J	57	1.38	63.1
LDW-SS2214-U	190 J	114	2.69	92.0
LDW-SSSP3-A	180	114	1.56	0.1
LDW-SS2090-D	150	114	3.24	83.9
LDW-SS2200-D	150	114	2.38	63.1
RP-20	150 J	114	3.78	89.2
LDW-SS2200-A	140	114	2.33	55.5
LDW-SS2201-A	140	114	1.70	67.2
LDW-SSBDC2-A	140	57	1.28	57.3
LDW-SS2090-A	130	114	3.32	81.7
LDW-SS2201-D	130	114	2.58	74.0
RP-25	130 J	57	1.92	67.8
LDW-SS2078-A	120 J	114	3.13	90.0
LDW-SS2078-D	120 J	114	3.27	61.7
LDW-SS2099-D	120 J	114	4.01	67.5
LDW-SSBDC3-D	120	114	1.66	60.6
RP-17	110	57	1.98	74.7
RP-12	66	57	2.66	59.7

Notes:

dw: dry weight

J: estimated concentration RAL: remedial action level TOC: total organic carbon



The history of benzyl alcohol exceedances in the upper reach of the LDW is consistent with the LDW-wide trends (Table A-3). There were no benzyl alcohol concentrations in the 0- to 10-cm samples in the RI/FS dataset that exceeded the SCO. After 2010, the detection frequency and number of SCO exceedances increased dramatically, with 48% of the samples having concentrations greater than the SCO. All benzyl alcohol exceedances in surface sediment in the upper reach (Map A-2) are associated with studies conducted after 2010.

Table A-3
Summary of Benzyl Alcohol Sediment Data in the Upper Reach of the LDW

Sediment Interval and Dataset	No. of Sediment Samples	Benzyl Alcohol Detection Frequency	No. of SCO Exceedances	Exceedance Frequency
0–10 cm – RI/FS	234	2%	0	0%
0–60 cm – RI/FS	25	12%	2	8%
0–10 cm – post-FS	128	77%	62	48%
0–60 cm – post-FS	5	100%	5	100%

Notes:

FS: feasibility study

LDW: Lower Duwamish Waterway

RI: remedial investigation

SCO: sediment cleanup objective

Analytical Improvements

In 2016, the U.S. Army Corps of Engineers (USACE) reviewed the changes in benzyl alcohol concentrations on behalf of the Dredged Material Management Program (DMMP) and concluded that the most likely cause of the dramatic increase in benzyl alcohol detections and concentrations since 2010 is changes in the analytical methods used for the analysis of semi-volatile organic compounds (SVOCs) (Fourie and Fox 2016). The changes in analytical methods include improvements in sample extraction methods, extract cleanup methods, and analytical technology, including chromatographic equipment and instrument conditions, such as injection port temperatures.

Benzyl alcohol is quantified as a SVOC using U.S. Environmental Protection Agency (EPA) method 8270. This method was developed for the analysis of non-polar organic compounds, such as polycyclic aromatic hydrocarbons and phthalates. Benzyl alcohol is more chemically reactive than these non-polar compounds, and laboratories have historically had difficulty with benzyl alcohol recoveries due to chromatographic interferences. Specifically, benzyl alcohol has a strong tendency to react with high-molecular-weight humic materials present in a sample.

In the 1990s, the standard sediment sample mass for SVOC analysis was large (60 to 100 g wet weight [ww]) compared to the mass required by current extraction protocols (20 to 30 g ww). The larger sediment masses were necessary to achieve the required sensitivity for target analytes. However, the large sample sizes also resulted in high levels of high-molecular-weight humic materials and other reactive materials. The presence of these potentially interfering compounds required additional cleanup steps that removed both the interfering compounds and the benzyl alcohol.

In order to increase the efficiency and sensitivity of their protocols, laboratories have developed protocols that enable them to reduce the sediment mass required for analysis. Less mass reduces the presence of humic materials that can cause matrix interferences in the sample extract. Fewer interferences reduces the need for post-extraction cleanup steps and improves the chromatographic performance of the sample. It appears that the improvements in laboratory protocols have resulted in the increased detections and concentrations of benzyl alcohol (Fourie and Fox 2016).

If the analytical method changes are responsible for the changes in benzyl alcohol detections and concentrations, then the 1986 sediment concentrations used to set the SCO were biased low relative to the results currently being reported. Therefore, an SCO exceedance based on current analytical methods is not directly comparable to an SCO exceedance in samples collected prior to the analytical method changes. As a result, the benzyl alcohol concentration at which toxicity occurs may be greater than the SCO when samples are analyzed with the updated analytical methods.

Toxicity of Benzyl Alcohol

The Washington State Sediment Management Standards allow a toxicity override when chemical sediment criteria are exceeded. This override is particularly important when chemistry results are subject to interpretation (e.g., different method, unusual mixture). Toxicity tests may also provide another line of evidence supporting the update of SCOs based on previous analytical methods.

In the upper reach of the LDW, bioassays have been conducted for 20 surface sediment samples (Map A-2). All of the samples, which were collected in 2011 as part of a sediment characterization study conducted in the vicinity of the former Rhone-Poulenc facility (Cardno Entrix 2012), passed all of the bioassays. The highest benzyl alcohol concentration that passed all three bioassays in surface sediment was 260 μ g/kg (Table A-4). This concentration is more than four times greater than the SCO of 57 μ g/kg.

Table A-4
Bioassay Results for Surface Sediment Samples Conducted in the LDW Upper Reach for Which Only Benzyl Alcohol Exceeded the SCO

Sample	Benzyl Alcohol Conc. (µg/kg)	Benzyl Alcohol Conc.> Benthic SCO?	Additional SCO Exceedance? 1	Amphipod	Larval	Polychaete	Overall	
Surface Sed	Surface Sediment							
IT1	14	no	no	pass	pass	pass	pass	
IT3	19	no	no	pass	pass	pass	pass	
IT7	43	no	no	pass	pass	pass	pass	
IT5	49	no	no	pass	pass	pass	pass	
IT11	65	yes	no	pass	pass	pass	pass	
BKG-2	68	yes	Yes – SVOC ²	pass	pass	pass	pass	
IT13	87	yes	Yes - PCBs	pass	pass	pass	pass	
IT8	93	yes	no	pass	pass	pass	pass	
IT6	96	yes	no	pass	pass	pass	pass	
IT14	100	yes	no	pass	pass	pass	pass	
BKG-6	110	yes	no	pass	pass	pass	pass	
IT9	110	yes	no	pass	pass	pass	pass	
IT10	110	yes	no	pass	pass	pass	pass	
BKG-1	120	yes	no	pass	pass	pass	pass	
IT2	120	yes	no	pass	pass	pass	pass	

	Benzyl Alcohol Conc.	Benzyl Alcohol Conc.>	Additional SCO				
Sample	(µg/kg)	Benthic SCO?	Exceedance? 1	Amphipod	Larval	Polychaete	Overall
BKG-3	170	yes	no	pass	pass	pass	pass
BKG-5	180	yes	no	pass	pass	pass	pass
IT12	220	yes	no	pass	pass	pass	pass
BKG-4	260	yes	no	pass	pass	pass	pass
IT4	260	yes	no	pass	pass	pass	pass
Subsurface	sediment						
DMMU 4	60	yes	no	pass	pass	pass	pass
DMMU 12	66	yes	no	pass	pass	pass	pass
DMMU 17	68	yes	no	pass	pass	pass	pass
DMMU 11	72	yes	no	pass	fail (SCO)	pass	pass
DMMU 5	82	yes	no	pass	pass	pass	pass
DMMU 7	86	yes	yes – PCBs³	pass	fail (SCO)	pass	pass
DMMU 10	91	yes	no	pass	pass	pass	pass
LDW13 2- 7.2C2	100	yes	no	pass	fail (CSL)	pass	fail
LDW16 0- 2.5C	130	yes	no	pass	fail (CSL)	pass	fail
DMMU 8	140	yes	no	pass	pass	pass	pass
DMMU 9	140	yes	no	pass	pass	pass	pass
LDW17 0- 3.5C	160	yes	yes - PCBs	pass	fail (CSL)	pass	fail
DMMU 6	200	yes	no	pass	fail (SCO)	pass	pass
LDW18 0- 2.8C	290	yes	no	pass	fail (SCO)	pass	pass

Notes:

Source: Cardno Entrix (2012) and Fourie and Fox (2016)

- 1. SCO exceedances for chemicals other than benzyl alcohol.
- 2. Sample also exceeded the SCO for 2,4-dimethylphenol, dibenzofuran, five individual PAHs, and total LPAH.
- 3. Primary sample had PCB concentration below the SCO, field duplicate sample exceeded the SCO for PCBs.

CSL: cleanup screening level

DMMU: dredged material management unit DMMP: Dredged Material Management Program

LDW: Lower Duwamish Waterway

LPAH: low-molecular-weight polycyclic aromatic hydrocarbon



PAH: polycyclic aromatic hydrocarbon

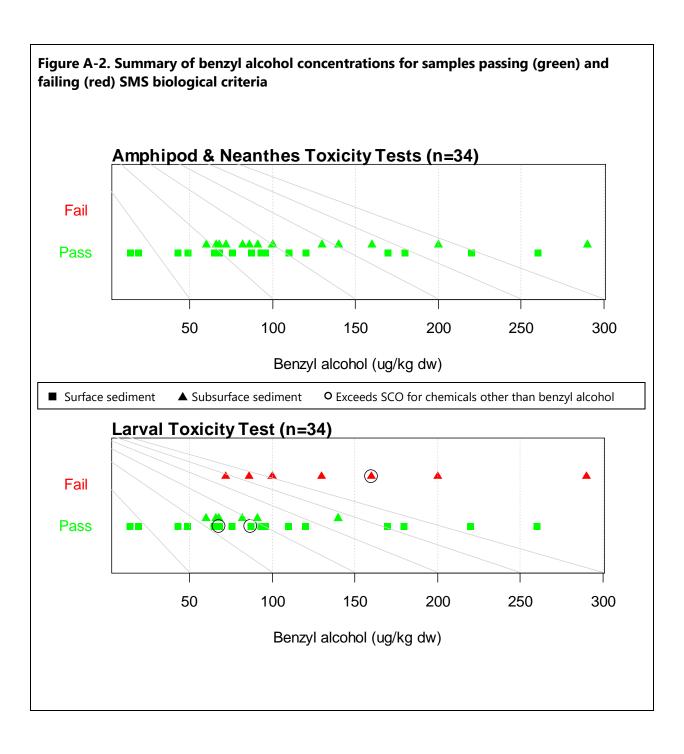
PCB: polychlorinated biphenyl SCO: sediment cleanup objective

SVOC: Semi-volatile organic compounds

In addition to the 20 surface sediment samples, 14 subsurface composite sediment samples were submitted for bioassay testing for dredge disposal decisions. The data for the subsurface samples are provided in Table A-3. The subsurface composites samples were collected by the ACOE to characterize shoal material throughout the LDW (USACE 2013) and for dredge material characterization in the Navigation Channel between RM 4.05 and RM 4.65 (USACE et al. 2018)(Map A-2².

² Only the shoal characterization locations are shown on Map A-1.

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Conclusions

The benzyl alcohol remedial action level (RAL) is set at the benthic SCO (in Recovery Category 1 areas) or two times the benthic SCO (in Recovery Category 2/3 areas). The sediment concentrations used to set the benthic SCO were lower than the concentrations that would be quantified today because of chromatographic interferences in the analysis of benzyl alcohol.

The Seattle District Dredge Material Management Program (DMMP) agencies (Ecology, USACE, EPA and Washington Department of Natural Resources) recommend re-evaluation of the benzyl alcohol DMMP guidelines in its 2016 clarification paper because they "do not believe that benzyl alcohol is a chemical of significant concern at the concentrations found in many dredging projects" using current analytical methods (Fourie and Fox 2016). Recent sediment samples from the LDW upper reach have had concentrations of benzyl alcohol similar to those discussed in the DMMP's clarification paper. A toxicity testing approach that considers this information will be outlined in the PDI QAPP or QAPP addendum.

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ATTACHMENT B TO APPENDIX C. EARLY ACTION AREA MONITORING DATA SUMMARY

Introduction

This attachment to the Pre-Design Investigation Work Plan (PDIWP) describes post-construction monitoring for the four early action areas (EAAs) in the upper reach of the Lower Duwamish Waterway (LDW) and summarizes data available within these EAAs. An understanding of current conditions in the EAAs will inform the sampling design and data interpretation for areas adjacent to EAAs. The data presented in this attachment are post-construction data within the EAA boundaries. The monitoring activities within the four EAAs in the upper reach are summarized in Table B-1. Sampling that occurred outside of the EAA boundaries (i.e., perimeter sampling) is included in the PDIWP discussions.

Table B-1
Summary of monitoring activities within EAAs in the Upper Reach

RM	EAA	Construction Complete	Monitoring Events	Sediment Intervals	COCs
			2015	0–10 cm (33 locations)	PCBs, PAHs, arsenic,
3.0-3.6 E	Boeing Plant 2	2015	2016	0–10 cm (33 locations)	dioxins/furans, other
	Tidit 2		2018	0–10 cm (33 locations)	SMS
3.5–3.7 W	T-117	2015	2019	0–10 cm (4 locations)	PCBs, PAHs, arsenic, dioxins/furans (2 locations), phenol
3.6–3.7 E Jorgensen Forge	Jorgensen	1 /014	2015	0–10 cm and 0–2 cm (19 locations) _a	DCPs motals
	Forge		Forge 2014	2016	0–10 cm, 0–60 cm, and 0–2 cm (19 locations) ^a
			1999	0–10 cm (4 locations) ^c	
			2000	0–10 cm (4 locations)	
4.9–5.0 E ^b No	Nowfalls	1000	2001	0–10 cm (4 locations)	PCBs, PAHs, arsenic,
	INOTIOIK		2002	0–10 cm (4 locations)	other SMS
			2003	0–10 cm (4 locations)	
			2004	0–10 cm (4 locations)	

Notes:

- ^a Jorgensen Forge identified 22 locations (Anchor QEA and Farallon 2016); 3 locations are outside the removal action boundary and not included here.
- The Boeing south storm drain removal, conducted in 2003, was also in this area. Monitoring for PCBs began in 2004; the most recent monitoring event was in 2017.
- ^c Includes only monitoring locations; additional sampling occurred in 2002, 2006, 2008, and 2011.

COC: contaminant of concern

EAA: early action area

PAH: polycyclic aromatic hydrocarbon

PCB: polychlorinated biphenyl

SMS: Washington State Sediment Management Standards



Boeing Plant 2

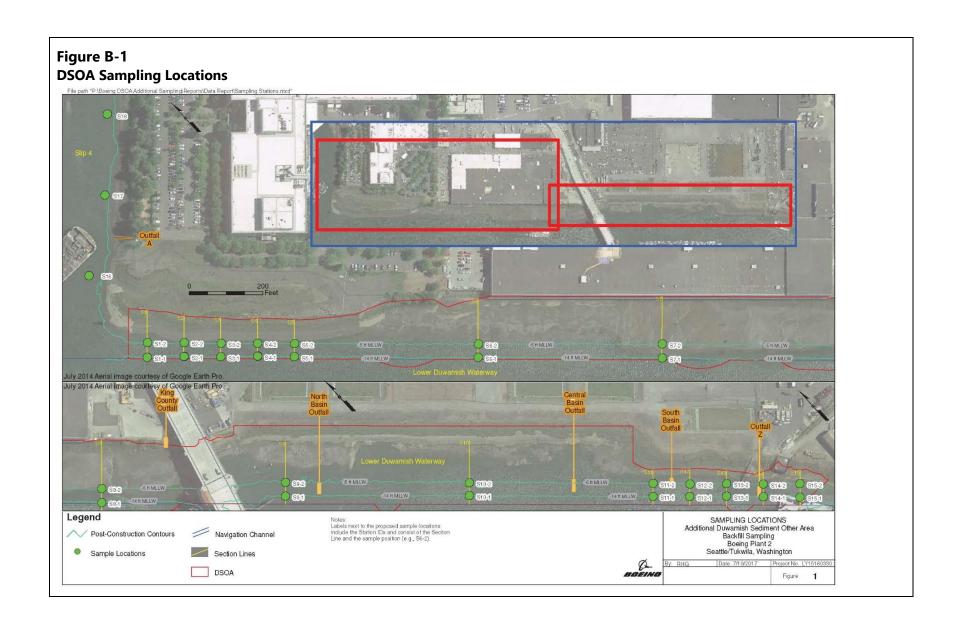
Construction was completed at the Boeing Plant 2 EAA in 2015, and the remediation achieved all stated objectives (AMEC Foster Wheeler et al. 2016). Under U.S. Environmental Protection Agency (EPA) oversight, The Boeing Company (Boeing) is conducting post-construction monitoring at the Boeing Plant 2 EAA. Boeing is collecting 0- to 10-cm sediment samples at 33 locations. These samples are being analyzed for Washington State Sediment Management Standards (SMS) analytes¹ and dioxins/furans. Results for Year 0 (2015), Year 1 (2016), and Year 3 (2018) analyses are currently available.² Total polychlorinated biphenyl (PCB) results are shown on Map B-1 and SMS chemical results with respect to benthic sediment cleanup objectives (SCOs) (WAC 173-204-562) are shown on Map B-2. Additional sampling will be conducted in 2020, 2022, and 2025 (Wood 2018).

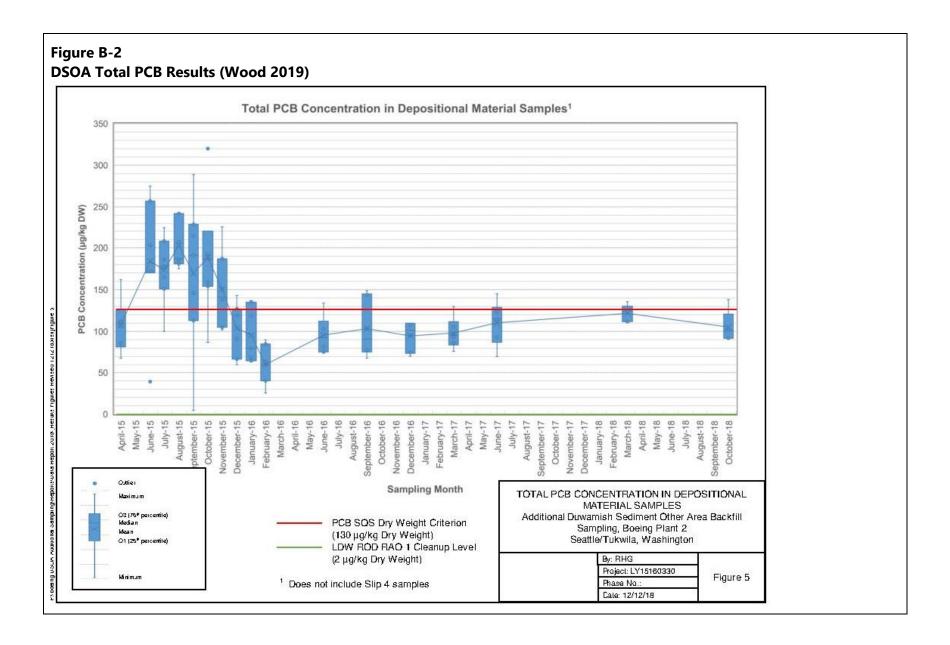
In addition to this monitoring, Boeing is performing voluntary monitoring at the Duwamish Sediment Other Area (DSOA) backfill area (Wood 2019). Dredging and backfill construction work was compeleted at the DSOA backfill area in March 2015. The samples in this area were collected between April 2015 and October 2018. Sample locations are shown on Figure B-1. These samples are representative of material that has accumulated on top of the DSOA backfill area cap; sample depths vary depending on the amount of sediment deposition that has occurred since the remedial action. The DSOA samples are being analyzed for conventional parameters and PCB Aroclors. Figure B-2 shows total PCB results for the depositional material as a function of time, Figure B-3 shows post-construction depositional material depths (i.e., surficial silt thicknesses) at sampling locations as a function of time, and Figure B-4 shows total organic carbon (TOC) results for the depositional material (Wood 2019).

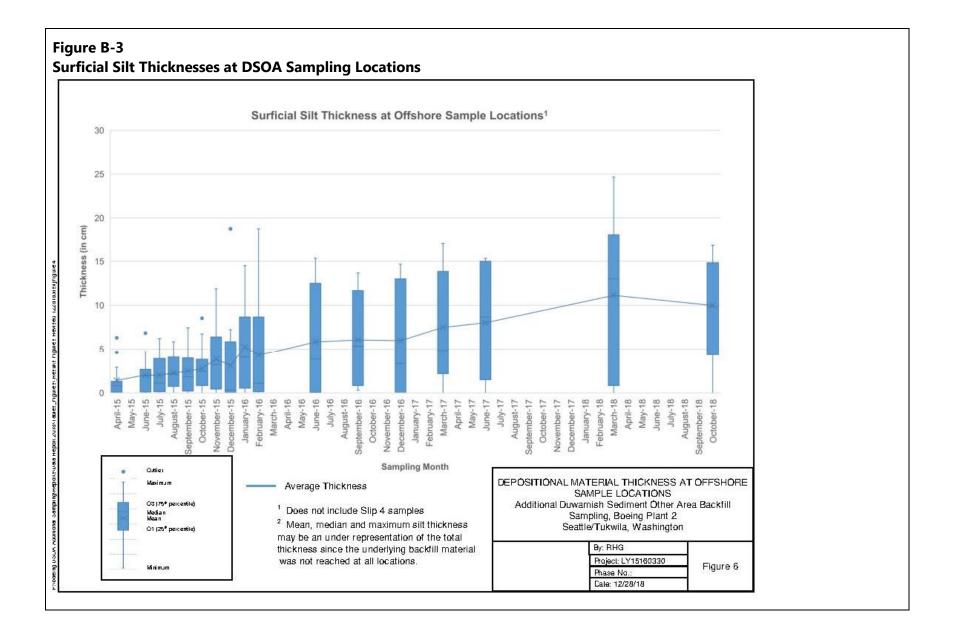
 $^{^2}$ Dioxin/furan TEQ results ranged from 0.0547 UJ (not detected at given estimated concentration) to 0.173 J (estimated concentration) ng /kg in Year 0 (2015), from 0.106 J to 1.28 J ng /kg in Year 1 (2016), and from 0.0547 UJ to 1.28 J ng /kg in Year 3 (2018).

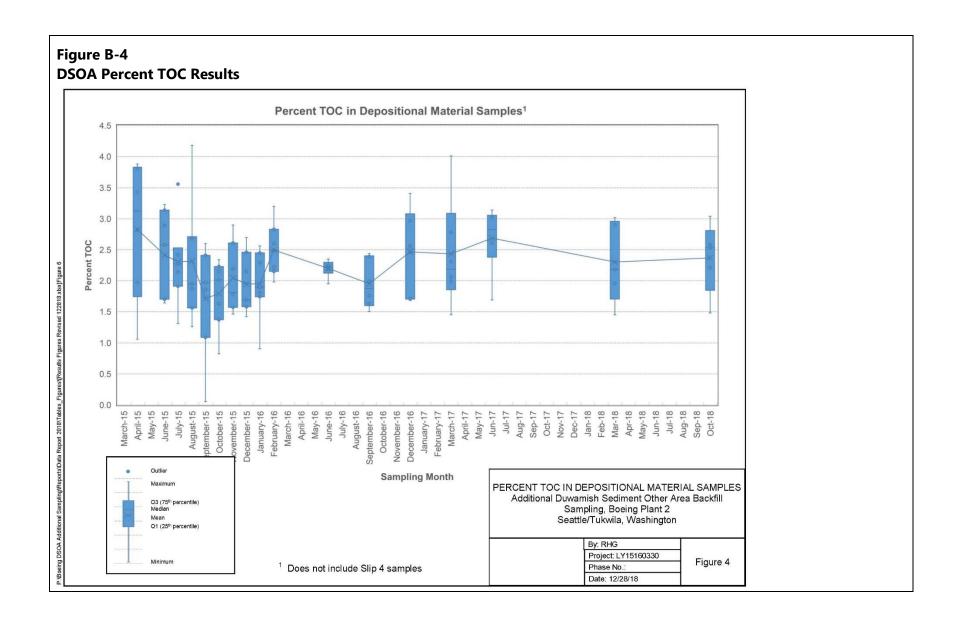


¹ These analytes include the 47 SMS analytes listed in Washington Administrative Code (WAC) 173-204-562., Other reported results include carcinogenic polycyclic aromatic hydrocarbon (cPAH) toxic equivalent (TEQ) and total polycyclic aromatic hydrocarbons (PAHs).









Jorgensen Forge

Construction at the Jorgensen Forge EAA was completed in 2014. The Earle M. Jorgensen Company (EMJ) conducted post-construction sediment sampling in 2015 and 2016. Additional sampling was conducted in spring 2019 at the Jorgensen Forge EAA;³ the data summary report containing the results of that sampling is expected in 2019. Additional remediation may be required for this site. In addition, five post-construction surface sediment samples were collected by Boeing in 2015 within the Jorgensen Forge EAA (Map B-3).

Post-construction total PCB results are shown on Map B-3 for all samples. The 0-10cm samples collected by Boeing and the Jorgensen 2016 surface sediment results are compared to the SMS on Map B-4. Within the EAA, 0- to 2-cm and 0- to 10-cm sediment samples were collected from 20 locations. In addition, sediment cores were collected in 2016 to characterize the 0- to 60-cm sediment interval.⁴

All of the samples were analyzed for total PCBs (Aroclors) and metals. PCBs were the only COC detected at concentrations above the benthic SCO.⁵ Sediment PCB concentrations were above the benthic SCO at seven locations (Map B-4). The total PCB concentrations in the 0- to 60-cm samples were all below the benthic SCO.

⁵ The benthic SCO of 12 mg/kg OC was the removal action level.



³ Locations of sediment sampling are unavailable.

⁴ Three of the samples collected during this effort were collected from intervals less than 60 cm deep (i.e., 0 to 18 cm, 0 to 32 cm, and 0 to 50 cm). Samples were collected from the 0- to 18-cm and 0- to 32-cm intervals in order to characterize the backfill material, which was placed to a depth of 18 and 32 cm, respectively, at these locations. The reason the 0- to 50-cm sample was not collected from the 0- to 60-cm interval is unknown.

Terminal 117

Construction was completed at the Terminal 117 EAA in 2015, and the remediation achieved all stated objectives (AECOM 2018). Sediment monitoring is being conducted at the Terminal 117 EAA. The first round of post-construction sediment monitoring sampling occurred in 2019. Additional sediment monitoring will occur in 2021, 2023, and 2025 (Integral and AECOM 2018). Samples were collected from the 0- to 10-cm interval at four locations within the dredge/cap area.

Samples were analyzed for arsenic, PAHs, phenol, PCBs, and conventional parameters; two samples were analyzed for dioxins/furans. Post-construction sediment PCB concentrations are shown on Map B-5. There were no exceedances of the benthic SCO (Map B-6) or the dioxin/furan remedial action level (RAL).

Norfolk

King County monitored four Norfolk EAA cap locations (NFK501, NFK502, NFK503, and NFK504) annually from 1999 to 2004 (Map B-7). In addition, three sediment samples were collected by the Washington State Department of Ecology (Ecology) in 2002, four locations were sampled as part of the LDW remedial investigation sampling in 2006, one sample was collected to characterize LDW upstream sediment in 2008, and three samples were collected by Ecology to characterize sediments in the vicinity of outfalls in 2011.

Adjacent to the Norfolk EAA, Boeing collected sediment samples from the 0- to 5-cm interval at two locations annually from 2010 to 2017 in the vicinity of the Boeing South storm drain outfall (Map B-6).

Post-construction total PCB results are shown on Map B-7. Sediment data are shown relative to benthic SCOs (WAC 173-204-562) on Map B-7. Benthic SCOs were exceeded for bis(2-ethylhexyl) phthalate, butyl benzyl phthalate, benzyl alcohol, PAHs, and total PCBs at least once during the monitoring (Maps B-7 and B-8).

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